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(54) POROUS BULK APATITE CARBONATE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a porous bulk apatite carbonate with a simple procedure free from the troubles of conventional production process by reacting a composition containing calcium carbonate with phosphoric acid under specific condition.

SOLUTION: This porous bulk apatite carbonate contains $\geq 0.5\text{wt.}\%$ of calcium carbonate and has a BET specific surface area of $\geq 10\text{m}^2/\text{g}$. The porous bulk apatite carbonate can be produced by reacting a substance containing calcium carbonate with phosphoric acid in a neutral region. The calcium carbonate-containing substance to be used as a raw material is preferably a natural material, especially shell. The average particle diameter of the porous bulk apatite carbonate can be controlled within the range of $1\text{--}50\text{ }\mu\text{m}$ by controlling the average particle diameter of the substance containing calcium carbonate to $0.5\text{--}20\text{ }\mu\text{m}$.

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CLAIMS

[Claim(s)]

[Claim 1]Porosity massive apatite carbonate characterized by a BET specific surface area being more than $10\text{-m}^2/\text{g}$ including calcium carbonate 0.5% of the weight or more.

[Claim 2]A manufacturing method of porosity massive apatite carbonate which makes it react to phosphoric acid in a neutral region, and manufactures the massive apatite according to claim 1 using a calcium carbonate inclusion.

[Claim 3]The manufacturing method according to claim 2 in which said calcium carbonate inclusion is a natural product.

[Claim 4]The manufacturing method according to claim 3 in which said calcium carbonate inclusion is a shell.

[Claim 5]The manufacturing method according to any one of claims 2 to 4 which controls mean particle diameter of massive apatite carbonate within the limits of 1–50 micrometers by controlling mean particle diameter of said calcium carbonate inclusion to 0.5–20 micrometers.

[Claim 6]By controlling reaction velocity, The manufacturing method according to any one of claims 2 to 5 which is what replaces (PO_4^{3-}) in an apatite expressed with chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ by (CO_3^{2-}) in 0.01–1 mol.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the method for manufacturing a porosity massive apatite useful as raw materials, such as a toothbrushing substrate, a perfume support agent, an antimicrobial agent, adsorbent, an adhesive composition, etc. besides vital implant materials, such as an artificial bone and an artificial tooth, and this porosity massive apatite.

[0002]

[Description of the Prior Art]Apatite carbonate, i.e., the apatite containing a carbonic acid group, A type which replaced some hydroxyl groups (OH^-) of chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ with the carbonic acid group (CO_3^{2-}), and B type which replaced a part of phosphate group (PO_4^{3-}) with the carbonic acid group are known. This apatite carbonate with the bone and gear tooth which constitute a human body from a point containing a carbonic acid group compared with hydroxyapatite (HAP) or tricalcium phosphate as a near material, It is used as a raw material of vital implant materials, such as an artificial bone and an artificial tooth, and also is used using the characteristic as raw materials, such as a toothbrushing substrate, a perfume support agent, an antimicrobial agent, and adsorbent. It is used also as add-in material of an adhesive composition as a new use in recent years (for example, JP,5-78632,A, JP,4-106177,A, etc.).

[0003]In manufacturing apatite carbonate, a dry method, wet process, etc. are known, but since there is character to excel in the low-temperature-sintering nature at the time of sintering apatite carbonate powder and manufacturing a living body implant material, wet process is used widely. And as a typical process in this wet process, it is common to make phosphoric acid (or phosphate) react to calcium salt in solution (for example, JP,5-78632,A, JP,4-106177,A, etc.). However, as for the apatite carbonate obtained by those methods, a particle size and carbonic acid content are limited by a manufacturing method. Since it was made to react on basic conditions in the above-mentioned wet process, the obtained apatite carbonate has a possibility that alkaline substances, such as calcium hydroxide, may remain.

[0004]The method of introducing the choke damp into a constructional system, making it react in a neutral region, and manufacturing apatite carbonate from such a thing, is also proposed. However, in such a method, since the airtight reaction vessel which can seal gas is needed and pH is adjusted to a neutral region using various kinds of buffers, it is necessary to remove the used buffer and the produced by-product.

[0005]On the other hand, as a raw material for manufacturing an apatite, UROKO of a shell and a fish, a fish, the bone of an animal, etc., The various proposal also of the art of exploiting effectively

the calcium carbonate content natural resources seldom exploited until now is made (for example, JP,63-107807,A, JP,7-303889,A, JP,7-277712,A, JP,8-104508,A, etc.). However, in these methods, it is fundamentally processed like the above-mentioned wet process, and the above-mentioned problem is solved.

[0006]

[Problem(s) to be Solved by the Invention] This invention is made under such a situation and the purpose, It is in providing the method of manufacturing by a simple procedure, and the apatite carbonate manufactured in this way, without producing a problem [in / for apatite carbonate useful as raw materials, such as an artificial bone, an artificial tooth and a toothbrushing substrate, a perfume support agent, an antimicrobial agent, and adsorbent, / conventional technology].

[0007]

[Means for Solving the Problem] This invention which was able to solve an aforementioned problem is porosity massive apatite carbonate which has a gist at a point that a BET specific surface area is more than $10\text{-m}^2/\text{g}$ including calcium carbonate 0.5% of the weight or more.

[0008] Porosity massive apatite carbonate of above-mentioned this invention can be manufactured by making it react to phosphoric acid in a neutral region using a calcium carbonate inclusion. As for a calcium carbonate inclusion as a raw material, it is preferred that it is a natural product, among these its shell is the most preferred.

[0009] Even if it uses that in which the mean particle diameter is 0.5-1000 micrometers, the purpose of this invention is attained, but said calcium carbonate inclusion used by this invention method. If mean particle diameter is controlled to 0.5-20 micrometers, since mean particle diameter of porosity massive apatite carbonate is controllable within the limits of 1-50 micrometers, it is useful.

[0010] (PO_4^{3-}) in an apatite expressed with chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ can be replaced by (CO_3^{2-}) in 0.01-1 mol by controlling reaction velocity.

[0011]

[Embodiment of the Invention] This invention persons inquired from various angles, in order to attain the above-mentioned purpose. As a result, if the above-mentioned calcium carbonate inclusion and phosphoric acid are made to react in a neutral region, Without [without it adds processing by acid or alkali, and] using various kinds of buffers, effectively, the reaction could be advanced, it found out that the porosity massive apatite carbonate possessing the characteristic of wishing was obtained, and this invention was completed. According to this invention method, that there is an advantage of following (1) and (2) also found out.

[0012] (1) By controlling the mean particle diameter of coal-for-coke-making acid calcium to 0.5-20 micrometers, the mean particle diameter of porosity massive apatite carbonate is controllable within the limits of 1-50 micrometers.

(2) By controlling reaction velocity, (PO_4^{3-}) in the apatite expressed with chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ can be replaced by (CO_3^{2-}) in 0.01-1 mol.

[0013] Probably this invention method can be considered as follows, although not the all could be solved about the reason a reaction advances effectively by this although characterized [greatest] by making a calcium carbonate inclusion and phosphoric acid react in a neutral region. That is, the phosphoric acid dropped into the calcium carbonate slurry reacts on the surface first, and generates an apatite. And the phosphoric acid dropped one by one reacts to the calcium carbonate eluted from the inside used as porosity, and grows up an apatite further toward the exterior. this

time -- disassembly of calcium carbonate -- generating (CO_3^{2-}) -- it exists near the growing point of an apatite and it is thought that competition substitution is carried out with (PO_4^{3-}) at the time of that crystal growth, and apatite carbonate is generated.

[0014]In this invention, "it is made to react in a neutral region" means that the great portion of reaction advances in the neutral region which is pH 6.0 to about 7.0, and the case where it inclines to the acidity side whose pH is about five rapidly at the time of ending reaction is also included (refer to the after-mentioned example).

[0015]Although the grinding articles (for example, calcium carbonate by incorporated company cull seed, calcium carbonate by Bihoku Funka Kogyo CO., LTD., etc.) of the calcium carbonate unearthed as an ore can also be used as a calcium carbonate inclusion used as a raw material by this invention, As a raw material with it, what ground the shell considering and [which can be obtained in large quantities], and the point of purity is the most preferred. [preferred among these using what ground natural calcium carbonate inclusions, such as a bone of an animal, and a shell, and] [industrial] These calcium carbonate inclusions can be used being able to be independent or mixing. As a bone of the above-mentioned animal, which thing of vertebrates, such as coelenterates, such as mollusks, such as a squid, and a sand worm, and a cow, may be used.

[0016]Since it will be preferred that it is 0.5 micrometers or more as for the particle diameter, and particle diameter will become expensive [the grinding expense of a raw material] in less than 0.5 micrometer, and a reaction will progress too much early and it will be hard to perform control if the calcium carbonate inclusion which ground [above-mentioned] takes reactivity into consideration, calcium hydrogen phosphate etc. may be generated. On the other hand, as for the maximum of the particle diameter of a calcium carbonate inclusion, if mean particle diameter of porosity massive apatite carbonate is carried out from a viewpoint that it is controllable within the limits of 1-50 micrometers, it is preferred that it is 20 micrometers or less, but as mentioned above, a thing of 1000 micrometers or less can also be used. For example, water is made suspended at a rate of 1 to 30%, it is considered as suspension (reaction mixture slurry), and this calcium carbonate inclusion is a phosphoric acid diluent (preferably) to this. About 10 to 80% is mixed and the porosity massive apatite carbonate of this invention is obtained by making it react at about 30-100 ** for 1 to 10 hours.

[0017]It is thought that the porosity massive apatite carbonate produced by performing it above becomes a real target with which the great portion of calcium carbonate (namely, unreacted calcium carbonate inclusion) is unevenly distributed in a center section with two-layer structure. That is, in this invention method, a reaction advances from the circumference of a calcium carbonate inclusion, and it becomes the porosity massive apatite carbonate to which calcium carbonate remained in the center section eventually and which is two-layer structure substantially. And the content including a calcium carbonate maldistribution portion will be about 0.5 % of the weight or more.

[0018]On the other hand, it is known that the shape of particle (morphology) and a BET specific surface area have correlation ****, For example, the BET specific surface area of a whisker or an aggregate (agglomerete) is more than $10 \text{ m}^2/\text{g}$, and less than $10 \text{ m}^2/\text{g}$ becomes in a fine grain (granule). That is, in the conventional manufacturing method, only the thing of the particle properties of whether it is detailed (that is, specific surface area, size) and a fine grain (that is, specific surface area, smallness) was obtained. On the other hand, the apatite carbonate powder concerning this invention serves as a massive fine grain of porosity with a as big BET specific surface area as more than $10 \text{ m}^2/\text{g}$.

[0019]By the way, what has a medicinal value in the inside of a shell is known, for example, the shell of an oyster is called an oystershell, and the powder is used as a medicine for Chinese medicine formulation. If the apatite carbonate obtained by this invention uses the shell with which an unreacted calcium carbonate inclusion is unevenly distributed in a center section and which has a medicinal value as a calcium carbonate inclusion since it is two-layer structure substantially, depending on the using form, such a medicinal value can also expect the apatite carbonate obtained. Next, an example is shown.

[0020]

[Example]

The apatite carbonate of this invention was manufactured on condition of the example 1 following.
reaction vessel: -- beaker raw material made from 3-l. stainless steel: -- the end of oyster shell powder (mean particle diameter: 9.1 micrometers)

Reaction-mixture slurry: Raw material 200g+ ion exchange water 1800g (slurry concentration: 10%)

Phosphoric-acid (H_3PO_4) liquid: The total dropping time required:5 hours of 30-% of the weight

concentration and 353g reaction temperature:70 ** phosphoric acid (a reaction is ended with the end of dropping)

Last pH: It was $23m^2/g$ when BET specific surface area ** of the apatite carbonate particles obtained 5.0 was measured by "BELSORP28" (made by Japan bell incorporated company). The X diffraction of this apatite carbonate particle was performed on condition of the following.

(X diffraction conditions)

X-ray-diffraction-analysis device : "RAD-1A" (made by Rigaku International Corporation)

measurement voltage: -- 35-kV measuring-electric-current: -- 15-mA sensitivity: -- 2000-cps damping time constant: -- 1-sec scan speed: -- 2 degrees / min [0021]An X diffraction result is

shown in drawing 1. The crystal structure of the obtained apatite carbonate is shown in drawing 2 (microphotograph for cost of blueprint). It can consider as follows from these. Although the portion shown by the arrow (**) in drawing 1 showed calcium carbonate, it has been judged from the peak intensity of this calcium carbonate portion that calcium carbonate in apatite carbonate was 10%.

[0022]The apatite carbonate of this invention was manufactured on condition of Example 2 - 4 following. In the following Examples 2-4, reaction velocity was changed by changing the total dropping time required, reaction concentration, and reaction temperature of phosphoric acid.

[0023]example 2 reaction vessel: -- beaker raw material made from 3-l. stainless steel: -- calcium carbonate (made by incorporated company cull seed) -- a ball mill -- feed-to-pulverizing-machine mean-particle-diameter: -- 0.8-micrometer reaction mixture slurry: -- the raw material 600g+ ion exchange water 1400g (slurry concentration: 30%)

Phosphoric-acid (H_3PO_4) liquid: The total dropping time required:1 hour of 50-% of the weight

concentration and 351g reaction temperature:60 ** phosphoric acid (a reaction is ended with the end of dropping)

Last pH: 5.1 [0024]example 3 reaction vessel: -- beaker raw material made from 3-l. stainless steel: -- charge mean-particle-diameter of hard clam shell flour Suehara: -- 5.3-micrometer

reaction mixture slurry: -- the raw material 400g+ ion exchange water 1400g (slurry concentration: 20%)

Phosphoric-acid (H_3PO_4) liquid: The total dropping time required:5 hours of 70-% of the weight concentration and 312g reaction temperature:70 ** phosphoric acid (a reaction is ended with the end of dropping)

Last pH: 5.0 [0025]example 4 reaction vessel: -- beaker raw material made from 5-l. stainless steel: -- calcium carbonate (made by Taihei Chemical Industrial Co., Ltd.)

mean-particle-diameter: -- 12.8-micrometer reaction mixture slurry: -- the raw material 150g+ ion exchange water 2850g (slurry concentration: 5%)

Phosphoric-acid (H_3PO_4) liquid: The total dropping time required:10 hours of 20-% of the weight concentration and 398g reaction temperature:90 ** phosphoric acid (a reaction is ended with the end of dropping)

Last pH: 5.2 [0026]About the obtained apatite carbonate particles, it analyzed by X-ray diffraction on the same conditions as the above. Mean particle diameter was measured with the laser diffraction type size distribution measuring device ["SALD1100" (Made by Shimadzu)], and 600 - 800 ** loss in quantity were analyzed with the differential thermal analyzer ["TAS-200" (made by Rigaku International Corporation)], and the calcium carbonate residue was measured. These X-ray diffraction analysis, mean particle diameter, and a calcium carbonate residue are shown in the following table 1 with a yield.

[0027]

[Table 1]

	X線回折分析	平均粒径 (μm)	炭酸カルシウム残量 (重量%)	収量 (g)
実施例2	HAP	2.7	0.7	594
実施例3	HAP + CaCO_3	13.3	5.8	387
実施例4	HAP + CaCO_3	25.3	12.6	145

[0028]With the above-mentioned laser diffraction type size distribution measuring device, the particle size distribution of end of precursor powder and output powder was measured. The result is shown in drawing 3 - 8. Namely, the particle size distribution [in / in drawing 3 / Example 2] in the end of precursor powder (calcium carbonate inclusion), Drawing 4 the particle size distribution of the output powder (apatite carbonate) in Example 2, Drawing 5 shows the particle size distribution of output powder [in / for the particle size distribution / in / for the particle size distribution of output powder / in / for the particle size distribution in the end of precursor powder in Example 3 / in drawing 6 / Example 3 / in drawing 7 / Example 4 / in the end of precursor powder / in drawing 8 / Example 4], respectively. Q (%) shows an integral value among drawing 3 - 8, and q (%) shows the differential value, respectively.

[0029]From the result shown in the mean particle diameter shown in Table 1, drawing 3 - 8, by controlling the mean particle diameter of a calcium carbonate inclusion shows that the mean particle diameter of massive apatite carbonate is controllable.

[0030]By the way, A type which replaced some hydroxyl groups (OH^-) of chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ with the carbonic acid group (CO_3^{2-}) as apatite carbonate was mentioned above, There is a B type which replaced a part of phosphate group (PO_4^{3-}) with the carbonic acid group, These can be identified by an infrared absorption spectrum and B type apatite carbonate can be expressed with general formula $\text{Ca}_{10-x}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_{2-x}$.

[0031]This invention persons performed identification of apatite carbonate and calcium carbonate using the infrared-absorption-spectrum device ["FT-IR"] (Made by Shimadzu). The following pitch was adopted as identification at this time.

(a) B type apatite carbonate : 1465-1412 (cm^{-1})

(b) Calcium-carbonate (calcite) : 712- cm^{-1} (c) calcium carbonate (ARAGO light) : 855- cm^{-1}

¹[0032]On the other hand, by CHN meter ["MT-3 type" (Made in Yanamoto Factory)], the whole quantity (CO_3^{2-}) was measured and the value which subtracted the calcium carbonate residue shown in said table 1 from this measured value was calculated as a quantity (CO_3^{2-}) replaced by (PO_4^{3-}). These results are shown in the following table 2 with the molecular formula of B type apatite carbonate which was able to be obtained.

[0033]

[Table 2]

	振動数 (cm^{-1})	(PO_4^{3-}) に置換した (CO_3^{2-}) 量 (mol)	分子式
実施例 2	1465, 1412, 712	0.03	$\text{Ca}_{9.97}(\text{PO}_4)_{5.97}(\text{CO}_3)_{0.03}(\text{OH})_{1.97}$
実施例 3	1465, 1412, 855	0.40	$\text{Ca}_{9.6}(\text{PO}_4)_{5.6}(\text{CO}_3)_{0.4}(\text{OH})_{1.6}$
実施例 4	1465, 1412, 712	0.92	$\text{Ca}_{9.08}(\text{PO}_4)_{5.08}(\text{CO}_3)_{0.92}(\text{OH})_{1.08}$

[0034]From these results, by controlling reaction velocity shows that (PO_4^{3-}) in the apatite expressed with chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ can be replaced by (CO_3^{2-}) in 0.01–1 mol.

[0035]

[Effect of the Invention]According to this invention, the following effect is acquired as stated above.

- (1) As apatite carbonate, particle diameter and carbonic acid content are controllable in the fixed range.
- (2) When using a shell as a carbonic acid cull SIMM raw material, it reacts not only in the negative reason of salvaging but in a neutral region, and the medicinal value which a shell has can also be expected by adjusting reacting weight and making an unreacted material remain.
- (3) Without [without it uses various kinds of buffers, and] also producing a by-product, since it is an easy manufacturing process, this invention method can be mass-produced.
- (4) The apatite carbonate concerning this invention is a porous body with big specific surface area. The apatite carbonate fine grain which was excellent in adsorption property can be obtained.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a graph which shows the X diffraction result of the apatite carbonate obtained in Example 1.

[Drawing 2]It is a microphotograph for cost of blueprint in which the crystal structure of the apatite carbonate obtained in Example 1 is shown.

[Drawing 3]It is a graph which shows the particle size distribution in the end of precursor powder in Example 2.

[Drawing 4]It is a graph which shows the particle size distribution of the output powder in Example 2.

[Drawing 5]It is a graph which shows the particle size distribution in the end of precursor powder in Example 3.

[Drawing 6]It is a graph which shows the particle size distribution of the output powder in Example 3.

[Drawing 7]It is a graph which shows the particle size distribution in the end of precursor powder in Example 4.

[Drawing 8]It is a graph which shows the particle size distribution of the output powder in Example 4.

[Translation done.]

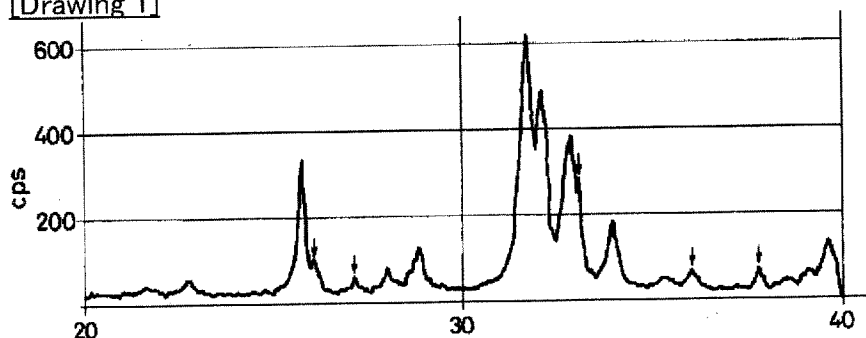
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DRAWINGS

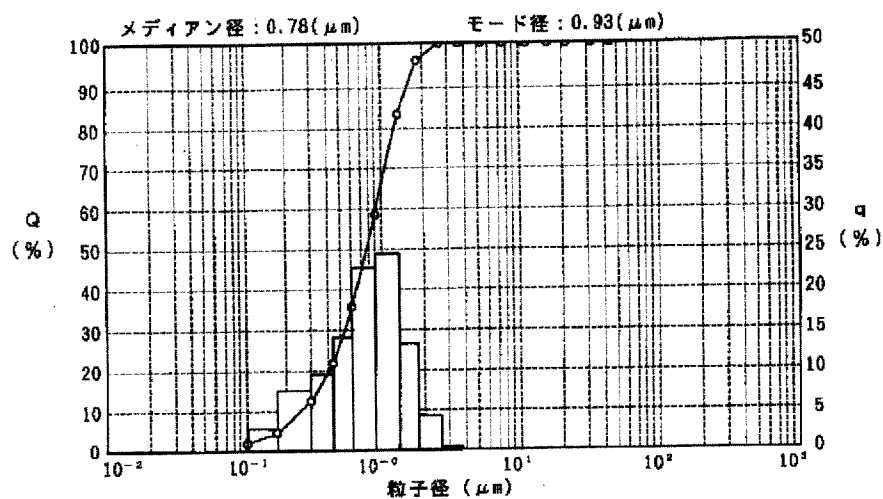
[Drawing 1]



[Drawing 2]

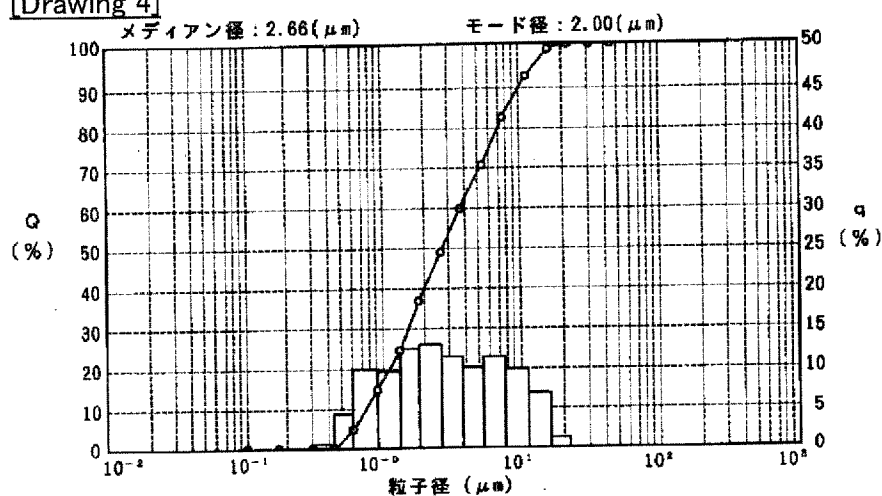


[Drawing 3]



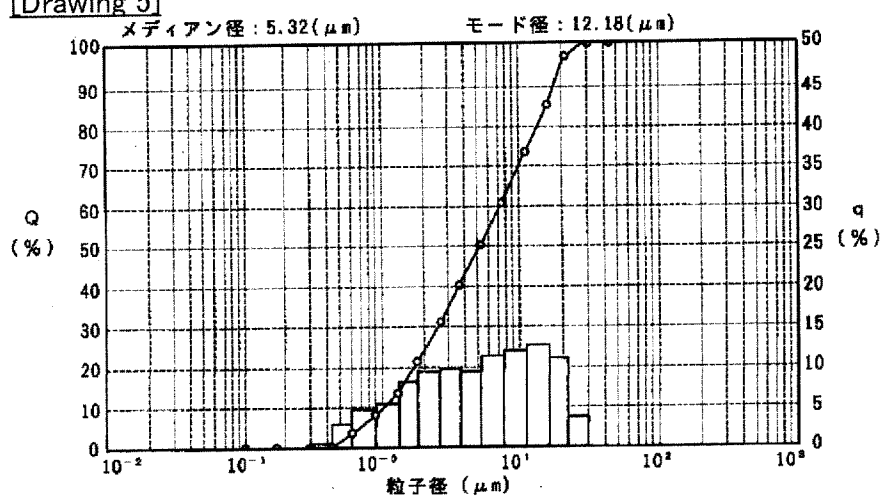
実施例 2 における原料粉末粒度分布

[Drawing 4]



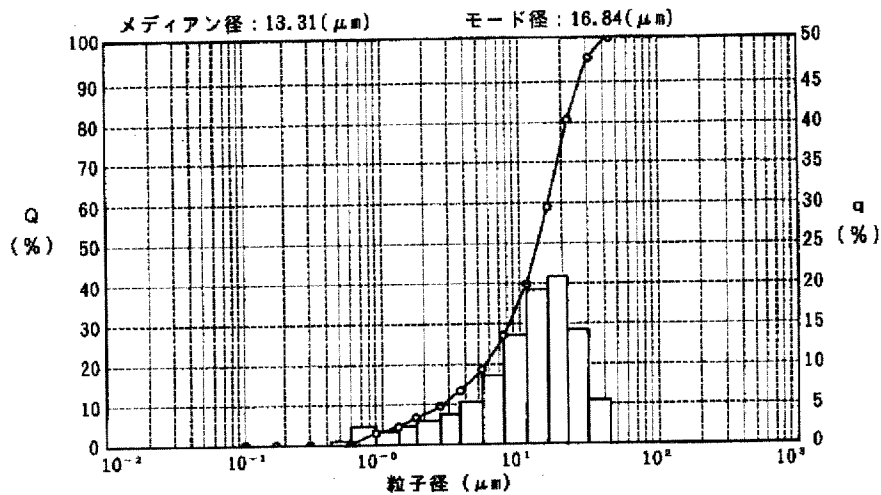
実施例 2 における生成物粉末粒度分布

[Drawing 5]



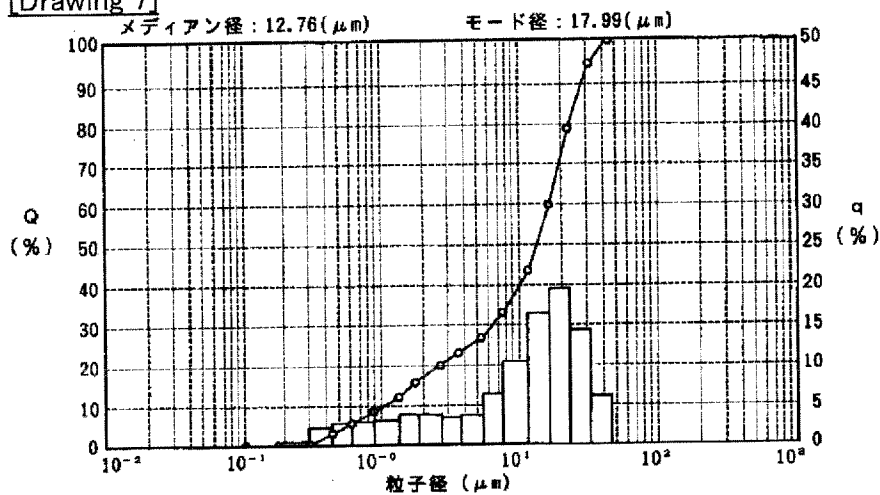
実施例 3 における原料粉末粒度分布

[Drawing 6]



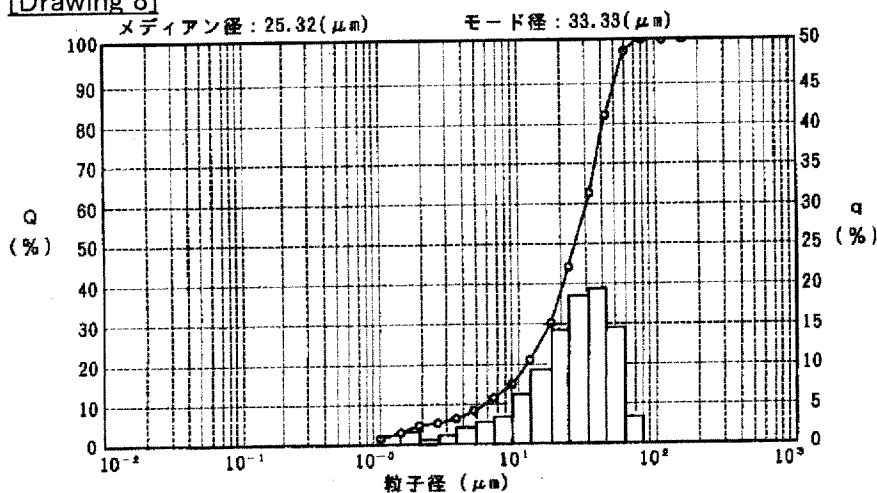
実施例 3 における生成物粉末粒度分布

[Drawing 7]



実施例 4 における原料粉末粒度分布

[Drawing 8]



実施例 4 における生成物粉末粒度分布

[Translation done.]